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By:

S. Ramesh, R. Shanti, Ezra Morris
and
R. Durairaj

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Exerted influence of DES concentration in the room temperature ionic conductivity and thermal behavior of CS-LiTFSI-DES polymer electrolytes.

S. Ramesh[a,*], R. Shanti[b], Ezra Morris[b], R. Durairaj[b]

[a] Centre for Ionics University Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[b] Faculty of Engineering and Science,

Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia

*rameshtsubra@gmail.com

* Corresponding author. Tel.: +603-79674391.

Abstract

In this communication, effort was devoted to fabricate completely biodegradable polymer electrolytes that are environmental-friendly by utilizing corn starch (CS), bis(trifluoromethanesulfonyl)imide (LITFSI) and deep eutectic solvent (DES) (synthesized from the mixture of choline chloride and urea with 1:2 ratio) by solution casting technique. The incorporation of DES in plasticizing the CS-LiTFSI matrix was valued primarily due to its capability in increasing the amorphous elastomeric phase in the polymer matrix. This is a new and versatile platform which allows high ionic conduction possessed by natural polymer based polymer electrolytes. In alien to identify the best DES composition ratio, a wide range of electrolyte compositions from 0 to 90 wt. % of DES was prepared by dissolution of DES in

CA-LiTFSI system. The resultant system was characterized by total ionic conductivity measurements, ions mobility and thermal analysis. The maximum conducting sample was identified with the DES content of 80 wt. % with the conductivity value of 1.04×10^{-3} S cm^{-1}. The stated sample was believed to have the highest ionic transport mechanism. A decreasing trend in the melting temperature of polymer electrolytes with increase DES content were visualized from the DSC analysis which suggest the complexation between the constituents that induce to structural disorderness. Relying on the TGA results, it can be visualized that the addition of an appropriate amount of DES in CS-LiTFSI matrix capable in sustaining both of its thermal properties as being desired.

Keywords: Ionic conductivity (σ); Conglomeration; Dissipation tangent loss (δ); Melting temperature (T_m); Thermal decomposition (T_d)

1. Introduction

The current worked out invention, has attracted scientific and practical interest in recent years due to the environmental pollution attributed to the massive load of non-degradable waste from synthetic polymer electrolytes. The only technique that can be manipulated to dispose this type of polymer electrolytes is through recycling which is neither practical nor economical. Thus, an effort was evolved in this communication by substituting with a type of natural polymer namely corn starch which was believed to be the best approach to render synthetic polymer electrolytes.

This effort could not be worked out by only utilizing the natural polymer due to its highly crystalline nature that inhibits its employment in the development of high conducting polymer electrolytes. Thus, corn starch based polymer electrolytes were developed with the combination of two different bio based materials namely LiTFSI and DES in order to obtain high conducting sample. This contraption was believed to exert applicable electrical and other promising properties as being desired. The selected hydrophilic polymer gain its interest due to number of listed outstanding properties such as its water solubility, availability of renewable resources, low cost, non-toxic and also due to its biodegradable nature [1-3].

Corn starch is a semi-crystalline polymer composed of both linear amylose and branched amylopectin chain [4]. In order to enable the natural polymer electrolytes to possess high ionic conductivity, the linear monomer chain arrangement needs to be disrupted as an initial effort allowing the matrix to present in highly amorphous state. The initial step was accomplished prior to the heating of CS in water which makes the starch granules become swollen and undergo disruption into smaller aggregates or particles which result in gelatinized corn starch [5-6]. At this point of time, amylose will be leached/secreted out from the starch granules which evident the diffusion in the amylose chain.

The second monomer that needs to be disrupted in order to further enhance the ionic transport mechanism is the short-chain fraction of amylopectin. This monomer was arranged as double helices in the form of highly crystalline order due to its branching nature [4, 7]. Thus, it is not easy to disorderliness the arrangement unless

disrupted by negatively charged ions (anions). In order to that, two different types of additives were used to obtain the anions for the disorderness purposes in this communication. The first anion that being relied was $TFSI^-$ obtained from the complete dissolution of LiTFSI in the polymer matrix. This type of anion is bigger in size thus it cannot contribute to greater structural disorderness which makes the CS-LiTFSI polymer electrolytes to exhibit low ionic conductivity.

In order to further disrupt the branched monomer, a highly negative charged ions was needed which is small in size to allow it to move in between the condensed arrangement of atoms more freely to enhance the amorphocity of polymer matrix. The referred anion is chloride (Cl^-) which was more electronegative than $TFSI^-$. The chloride ion was obtained from the ionic mixture synthesized from choline chloride and urea in a specific ratio [8]. This type of ionic mixture gains its interest due to some of its unique properties including its unusual solvent property that further dissolves the highly crystalline CS, cheap in cost compared to the ionic liquid due to the low cost of raw materials, ease in the preparation method ignoring the purification process and no medium being required, most of the formulations are non-toxic and even biodegradable [9-11]. This piece of effort enables the DES-plasticized sample to possess high ionic conductivity as being required for the application in electronic devices as listed namely fuel cells, solar cells, electrochromic windows, and solar-state batteries [12-16].

In this communication, the victory of the employed method to suppress the highly crystalline nature in CS matrix was scrutinized in terms of the room

temperature ionic conductivity, dissipation tangent loss and thermal properties behaviour.

2. Experimental

Materials

The selective corn starch that being used in this research work was purchased from Aldrich whereas LiTFSI were obtained from Fluka. The ionic mixture that being synthesized was composed of choline chloride and urea which were purchased from Sigma. Distilled water has been chosen as the suitable solvent in the effort to develop environmental-friendly polymer electrolytes.

Preparation of polymer electrolytes

1) Synthesizing ionic mixture

The respective ionic mixture was synthesized by heating up the mixture of two individual solids which are choline chloride and urea in the ratio of 1:2 under manual stirring condition using a hot plate. Upon the synthesizing process, those solid form chemicals will completely dissolve and appears as a colorless viscous solution.

2) Sample preparation

The initial step in developing the corn starch based polymer electrolytes were achieved by dissolving an appropriate amount of CS powder in distilled water

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and the resultant milky solution were heated up till the temperature of 75 °C in order to gelatinize the corn starch. This step will yield a transparent viscous solution.

After the heating process, the solution was then being cooled down at ambient temperature under constant stirring for about 30 minutes. Then an appropriate concentration of LiTFSI and the synthesized DES were added into the viscous solution and again the solution being allowed to stir for another an hour to allow a good miscibility between the added chemical constituents. The polymer electrolytes were then being casted by spreading the viscous solution on a clean Teflon plate and dry it in the oven at 55°C for 8 hours.

Instrumentation

Impedance spectroscopy

The thickness of the samples were measured with the aid of micrometer screw gauge before the samples being sandwiched in between the two stainless steel blocking electrodes with an area of 4.9807 cm^2 prior to impedance measurements. The analysis was performed by using HIOKI Model 3532-50 Hi-Tester over the frequency range from 50 Hz to 5 MHz. The Cole-Cole impedance plot will be attained upon the completion of the analysis. This plot was then based to obtain the bulk resistance (R_b) value in order to calculate the exerted ionic conductivity of polymer electrolytes by substituting in the equation below:

$$\sigma = L / R_b A \quad (1)$$

where σ is the conductivity in S cm^{-1}, L refers to the thickness of thin film sample in cm, R_b is the bulk resistance in Ω obtained from Cole-Cole impedance plot whereas A represent the surface area of the stainless-steel blocking electrodes in cm^2. Similar Cole-Cole impedance plot were relied upon obtaining the dissipation tangent loss plot.

DSC analysis

The melting temperature of the prepared samples was visualized by using DSC with the model of METTLER TOLEDO DSC823^e. The analysis were run by using an approximate of 5 mg of sample which were sealed in the aluminium standard 40 µL under an inert environment with the nitrogen flow rate of ca. 50 ml/min. The sample was heated sequentially from 25 °C to 500 °C at the heating rate of 10 °C/min.

TGA analysis

The thermal properties of polymer electrolytes were obtained by using the Mettler Toledo analyzer that consisted of TGA/SDTA851^e main unit and STARe software. This analysis was carried out at the temperature range of 25 °C to 550 °C with the heating rate of 10 °C min^{-1} under nitrogen atmosphere.

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3. Results and discussion

3.1. Ionic conductivity studies at room temperature

The variation of ionic conductivity possessed by CS-LiTFSI-DES polymer electrolytes as function of DES concentration was summarized in Table 1. For the ease in explaining the exerted ionic conductivity trend the values were sub divided into four individual regions.

The effectiveness of DES in increasing the amorphocity of CS-LiTFSI matrix was evident through the observed enhancement in the ionic conductivity with the minimum addition of DES concentration as being revealed at the first stage in Region 1 and this property further being improved with the addition of 20 wt. % of DES. The observed finding correlates to an increase in the concentration of free mobile ions which disrupts the ordered arrangement in CS matrix leading to an increase in the amorphous structure (highly disordered) [17]. The associated increment in the amorphocity allows extensive presence of free volume in between the polymer chains wherein increases the lithium ion (Li^+) transport mechanism through the polymer backbone.

In reference to Region 2, an initial abrupt drop in ionic conductivity was observed for electrolyte composting 30 wt. % of DES. The observed slump was attributed to the presence of neutral ion multiples as a result of the excess presence of DES particles [18]. This phenomenon was clearly been understood in terms of the conglomeration process. The associated ion aggregates will reduce the polymer-ionic mixture interface and hence blocks the existing conducting pathways

[19-20]. Thus, the ionic transport mechanism will be restricted and subsequently decrease the ionic conductivity. The ionic conductivity value was further being improved for sample IL-40 and this evident the dissociation of initially formed ion aggregates into free ions which again recreates the conducting pathways for better ionic transportation [18].

Ensue to the third region, a considerable increment in the ionic conductivity was initially observed for sample IL-50 before a drastic improvement being observed for sample containing 60 wt. % of DES. The increment in ionic conductivity shares the similar reasoning as in Region 1. Conversely, the drastic increment in ionic conductivity provides an insight on the radical increment in the structural disorderliness which induces to the presence of high amorphous fraction in the material which significantly improves the ion transport mechanism. The addition of ionic mixture above 60 wt. % results to an almost constant increment in ionic conductivity before a slight decrease in this property being observed as in Region 4. The reasoning for the drop was similar as earlier discussed in Region 2.

Overall it can be understood that DES is a potential candidate in increasing the amorphous fraction in CS-LiTFSI matrix evident from the extensive improvement in the ionic conductivity from 1.11×10^{-5} S cm^{-1} (non-plasticized sample) till it hits the maximum conducting point of 1.04×10^{-3} S cm^{-1} at room temperature for sample IL-80.

3.2. Dissipation tangent loss studies

Figure 1 sheds some light on the ionic transport mechanism in CS matrix when different DES concentration that being incorporated in CS:LiTFSI system. The appearance of peak both in non-plasticized and plasticized samples reveals the presence of relaxation dipoles in all the tested samples [21]. This observation confirms the conversion of the incorporated DES particles into free ions upon the complexation with CS-LiTFSI system which involved in the ion conduction.

The reallocation of peaks either to a higher or lower frequency provides an insight on the structural alternation prior to the addition of different DES concentration in polymer electrolytes. This information can be inferred by taking into account the maximum peak frequency of sample DES-0 as reference. Based on the graph it can be visualized that the peak was reallocated to lower frequency after the addition of 30 wt. % of DES. This shifts in peak correlates to the restriction in free ions mobility which was ascribed to the blocking of existing conducting pathways. Thus, a reduction in ionic conductivity will be observed since the extent of cations movement are the predominant factor in exerting high ion conduction. This shifting phenomenon also provides the knowledge on the increase in the relaxation time that possess by the free ions in the particular sample.

Further incorporation of 60 wt. % of DES in polymer electrolytes contributes to the reallocation of peak at higher frequency. This observation illustrates that the free ions experiences greater acceleration on its mobility at higher DES concentration which induces to an increment in structural disorderness. Thus, more free volume

will be available for the ease in the free ions mobility that contributes to an increase in the ionic conductivity. This shifting phenomenon also gives the knowledge on the reduction in the relaxation time that possess by the free ions at higher DES content [21].

3.3. Differential Scanning Calorimetry (DSC)

The respective melting temperature of pure CS, DES-0, DES-50 and DES-60 were summarized in Table 2 and the exhibited variation provides an insight on the constituent's miscibility in which influences the structural properties. It was observed that the concern parameter being altered prior to the miscibility of LiTFSI and DES.

The reduction in the melting temperature of DES-0 compared to the one observed in pure CS reveals the possible interaction between CS and LiTFSI [22]. The outcome of this interaction persuades to the disruption in the available crystalline fraction which increases the amorphocity of polymer electrolytes and allows the matrix to melt at lower temperature.

Further decrement in melting temperature being observed upon the incorporation of 50 wt. % of DES in polymer electrolytes. This finding evident the occurrence of complexation between DES in CS-LiTFSI matrix. The observed decline in melting temperature was attributed to the enhancement in structural disorderness which increases the fraction of amorphous region. Since there is greater availability of free volume between the connected molecules that were present

in amorphous region, thus a small amount of heat will be sufficient enough to overcome the weak bonding in order to melt the amorphous natured polymer matrix. Hence, a reduction in the melting temperature will be observed as more DES concentration being incorporated in the polymer electrolytes associated to an immense interaction that enhances the amorphocity of polymer electrolytes matrix.

In view of the results, it can be notified that the melting temperature of polymer electrolytes being reduced as more DES concentration being incorporated. This verifies the complete miscibility of ionic mixture in CS-LiTFSI matrix which induces to an extent of structural disorderliness.

3.4. Thermogravimetric Analysis

Knowledge on the influence of both LiTFSI and DES concentration on the CS matrix thermal properties was evaluated by the overlaid thermogravimetric curves of pure CS, DES-0, DES-40 and DES-80 as being represented in Figure 2. Some filtered information from Figure 2 on the total weight loss and maximum decomposition temperature has been recapitulated in Table 3.

Based on Figure 2 (b), an improvement in both the thermal stability and heat-resistivity of pure CS were observed prior to the incorporation of ionic salt, LiTFSI. The observed enhancement in heat-resistivity was correlated to the decomposition of the organic part in LiTFSI which induces to the displacement of the maximum decomposition temperature to a higher level. Since it is heat stable thus less monomer will be detached from the complex structure thus lower total weight

loss being observed.

The thermal properties further being altered upon the addition of DES in polymer electrolytes. Based on Figure 2 (c - d), it can be notified that the DES plasticized polymer electrolytes exhibited weight lost starting at the temperature of 100 °C, which were almost 200 °C lower than those experienced by non-plasticized sample as in Figure 2 (a - b). These characterizations reveals that the crystalline structures of the plasticized samples were not sustained due to the good miscibility of ionic mixture in CS-LiTFSI matrix.

Reference to the total weight loss experienced by sample DES-40, it reveals that the initial addition of DES in CS-LiTFSI system further improves the thermal stability of the polymer electrolytes. Wherein this effort tends to reduce the heat-resistivity of the respective samples through the observation on the decline in the maximum decomposition temperature. The diminishes in heat-resistivity property reasonably explains the possible structural disorderness in CS matrix that leads to the existence of vast free volume between the connected molecules which results in weaker bonding. Apparently, small amount of heat will be sufficient enough to disrupt the weak interactions between the connected molecules that were present in the amorphous region and hence decompose at lower temperature.

Further increase in DES content leads to the decline in both the thermal properties. This was associated to the presence of greater amorphous phase in the respective sample making it to be more heat sensitive. Thus, reduction in heat-resistivity will be observed companied by the increment in total weight loss as

more DES particles being eliminated out from the polymer electrolytes matrix upon the heating process [23].

4. Conclusion

High conducting 'green' polymer electrolytes were synthesized by plasticizing the CS-LiTFSI matrix with DES. The nature of DES capable in suppressing the crystalline elastomeric phase in natural polymer enabling more diffusion in the matrix. Herewith, lithium ion co-ordination takes place predominantly in the amorphous domain allowing the polymer electrolytes to possess high ambient temperature conductivity. In this system, the maximum enhancement in the ionic conductivity was achieved when incorporate 80 wt. % of DES in CS-LiTFSI matrix with the value of 1.04×10^{-3} S cm^{-1}. This particular sample composition being the highest conducting sample due to immense movements of lithium ions in vast amorphous region. The melting temperature of polymer electrolytes decreases with an increase in the DES concentration based on the DSC scrutiny. The knowledge on the polymer electrolytes thermal behavior was reviewed by the TGA analysis whereby the incorporation of selective low concentration of DES capable in increasing the thermal stability of the sample and this property diminishes in high DES containing samples.

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Table Captions

Table 1: Variation of room temperature ionic conductivity when different amount of DES being incorporated in CS:LiTFSI:DES polymer electrolytes.

Table 2: Observation on the changes in the melting temperature (T_m) when different amount of DES being incorporated in CS:LiTFSI matrix.

Table 3: Decomposition temperatures and percentages of total weight loss of pure CS, DES-0, DES-40 and DES-80 by TGA analysis.

Figure Captions

Figure 1: Variation of tan δ with frequency for samples DES-0, DES-30 and DES-60 at room temperature.

Figure 2: Thermogravimetric curves for pure CS, DES-0, DES-40 and DES-80.

Tables:

Table 1: Variation of room temperature ionic conductivity when different amount of DES being incorporated in CS:LiTFSI:DES polymer electrolytes.

Designation	Polymer electrolytes (CS: LiTFSI: DES), (wt. %)	Ionic conductivity, σ (S cm^{-1})	Region
DES-0	70.0 : 30.0 : 0.0	1.11×10^{-5}	1
DES-10	63.0 : 27.0 :10.0	1.47×10^{-5}	
DES-20	56.0 : 24.0 : 20.0	2.77×10^{-5}	
DES-30	49.0 : 21.0 : 30.0	8.37×10^{-6}	2
DES-40	42.0 : 18.0 : 40.0	3.98×10^{-5}	3
DES-50	35.0 : 15.0 : 50.0	6.18×10^{-5}	
DES-60	28.0 : 12.0 : 60.0	8.03×10^{-4}	
DES-70	21.0 : 9.0 : 70.0	8.70×10^{-4}	
DES-80	**14.0 : 6.0 : 80.0**	**1.04×10^{-3}**	
DES-90	7.0 : 3.0 : 90.0	9.94×10^{-4}	4

Table 2: Observation on the changes in the melting temperature (T_m) when different amount of DES being incorporated in CS:LiTFSI matrix.

Sample	Melting temperature, T_m (^oC)
Pure CS	313.36
DES-0	291.12
DES-50	257.57
DES-60	236.69

Table 3: Decomposition temperatures and percentages of total weight loss of pure CS, DES-0, DES-40 and DES-80 by TGA analysis.

Sample	Maximum decomposition temperature, T_d (°C)	Total weight loss, wt (%)
Pure CS	317.56	86
DES-0	406.67	82
DES-40	382.50	80
DES-80	261.45	88

Figures:

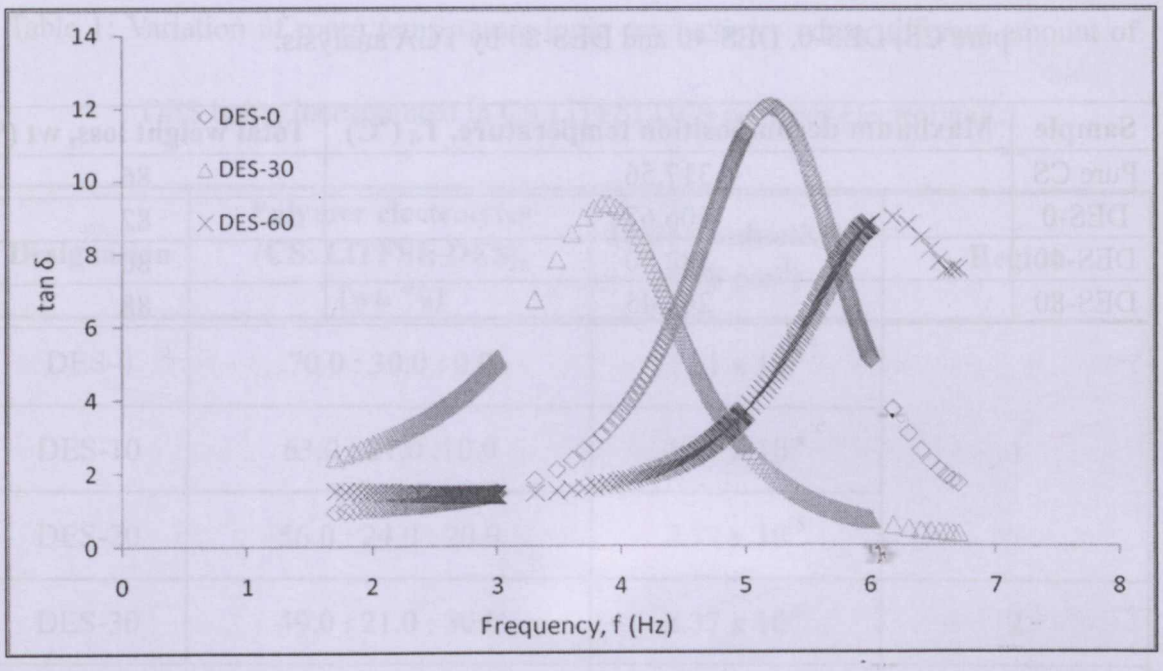

Figure 1: Variation of tan δ with frequency for samples DES-0, DES-30 and DES-60 at room temperature.

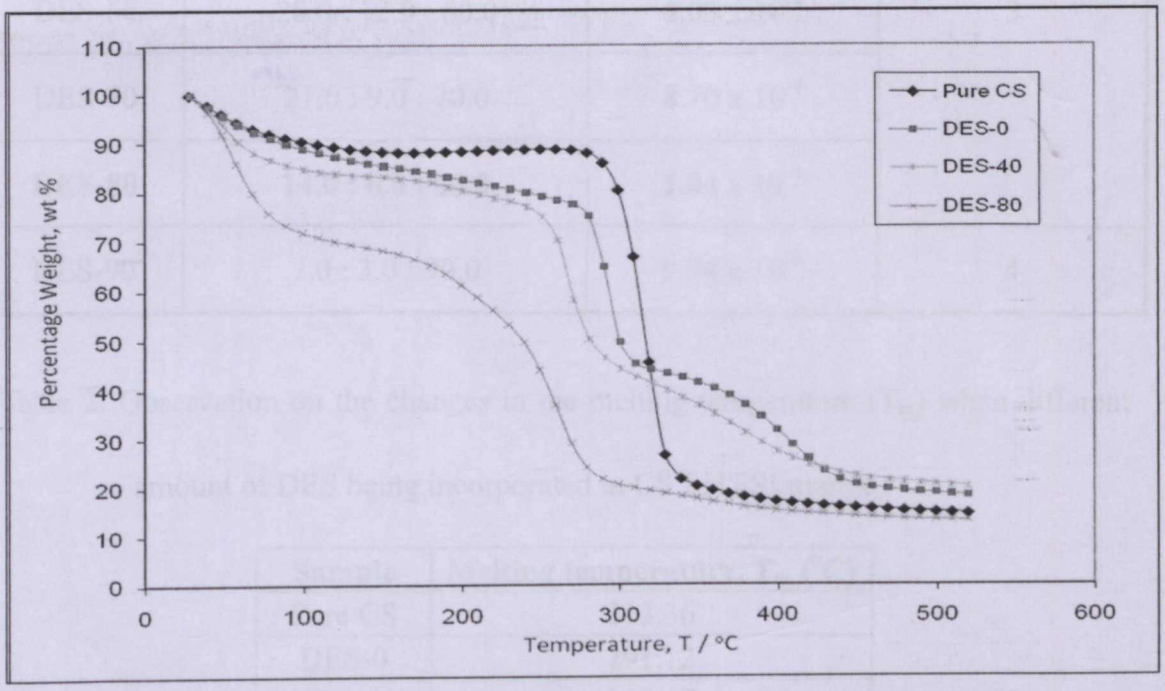

Figure 2: Thermogravimetric curves for pure CS, DES-0, DES-40 and DES-80.